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(21) International Application Number: PCT/EP98/03224 (22) International Filing Date: 29 May 1998 (29.05.98) (30) Priority Data: 97109295.2 9 June 1997 (09.06.97) EP (34) Countries for which the regional or international application was filed: DE et al. (71) Applicant: IMPERIAL CHEMICAL INDUSTRIES [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventors: SMITH, Richard, Colin; Vossekoten 20, B-3090 Overijse (BE). HUNNS, Jeremy, Charles, Bausor; 15 Applefield, Northwich, Cheshire CW8 4TE (GB). (74) Agents: NEVARD, Edward, John et al.; ICI Europe Ltd, ICI Polyurethanes, Intellectual Property Dept., Everslaan 45, B-3078 Everberg (BE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR THE PRODUCTION OF ORGANIC ISOCYANATES (57) Abstract <p>Process for the production of organic isocyanates comprising the following steps: (1) reacting an amine compound with an organic carbonate in the presence of a catalyst and an organic solvent; (2) removing the catalyst; (3) thermally decomposing the solution of the carbamate formed in step (1) in said organic solvent; and (4) separating the organic solvent/alcohol mixture thus obtained from the organic isocyanate formed in step (3) by distillation.</p>		

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Process for the production of organic isocyanates

The present invention relates to a multi-step process for the production of organic isocyanates from amines and organic carbonates using a common solvent.

The preparation of isocyanates starting from amines and organic carbonates is known.

5 US-A 5.315.034 discloses a multistep process for the preparation of alkyl mono- and diisocyanates by reacting the corresponding aliphatic amine or diamine with dimethylcarbonate in the presence of a basic catalyst, neutralising the catalyst, removing the alcohol and any excess of dimethylcarbonate, partially vaporizing and converting the urethane groups thus formed into isocyanate groups by cracking, subjecting the cracking products to fractional distillation at reduced
10 pressure and optionally recycling the unconverted part to the partial vaporization step.

The described method involves vaporization of the urethanes and fractional distillation at reduced pressure and hence does not allow for the preparation of involatile isocyanates.

EP-A 323.514 describes a two-step reaction for the preparation of diisocyanates consisting of first
15 reacting a diamine and dimethylcarbonate in the presence of an alkali catalyst and then thermally decomposing the thus formed urethane compound in a high boiling solvent under reduced pressure in the presence of a specific metal catalyst to obtain a diisocyanate compound.

The second step of this reaction requires the presence of a specific catalyst and a high boiling solvent and is carried out under reduced pressure. The process can only be used for the
20 production of difunctional isocyanates.

In DE-A 4.413.580 a method for preparing 1,4-diisocyanatobutane is described by converting 1,4-butanediamine into the corresponding dialkyl- or diarylurethanes which are subsequently thermally cracked at a temperature of between 100 and 600 °C into 1,4-diisocyanatobutane and
25 an alcohol, with fractional condensation of the cracking products.

This is a process for making a specific difunctional isocyanate which includes fractional condensation of the reaction products.

An improved method has now been found for the preparation of organic isocyanates by reaction of amines with organic carbonat s.

30 The invention thus concerns a process for th production of organic isocyanat s comprising the following steps :

- (1) reacting an amine compound with an organic carbonate in the presence of a catalyst and an organic solvent;
- (2) removing the catalyst;
- (3) thermally decomposing the solution of the carbamate formed in step (1) in said organic solvent; and
- (4) separating the organic solvent/alcohol mixture thus obtained from the organic isocyanate formed in step (3) by distillation.

The invention thus provides an efficient process for making any organic isocyanate, including higher boiling isocyanates.

10

Amine compounds which can be used in step (1) of the present process include aliphatic, cycloaliphatic or aromatic mono-, di- or polyamines.

Suitable amines include, for example, methylamine, ethylamine, n-propyl amine, isopropylamine, n-butylamine, isobutylamine, hexylamine, cyclopropyl amine, cyclobutylamine, cyclohexylamine, 15 laurylamine, stearylamine, phenyl amine, 4-chlorophenylamine, 2-fluorophenyl amine, 3,4-dichlorophenylamine, aniline, benzylamine, tolylamine, diisopropyl phenylamine, 2,4'-diamino diphenylmethane, 4,4'-diaminodiphenylmethane, 2,2'-diaminodiphenylmethane and high homologs (polyaminopolyphenylmethanes), 2,4-toluenediamine, 2,6-toluenediamine, m-phenylenediamine, 1,4-butylenediamine, 1,6-hexylene diamine, 1,5-naphthylenediamine, 20 1,4-cyclohexylenediamine, isophorone diamine, 2,2,4-trimethylhexamethylenediamine and mixtures thereof.

Preferred are aromatic di- or polyamines like toluenediamines, diaminodiphenylmethanes or polyaminopolyphenylmethanes or any mixtures thereof.

25 Suitable organic carbonates include cyclic or alicyclic carbonates such as, for example, ethylene carbonate, propylene carbonate, styrene carbonate, diphenyl carbonate, methyl phenyl carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, dihexyl carbonate, methyl ethyl carbonate, methyl butyl carbonate and the like.

The polyamines and the organic carbonates may be reacted in stoichiometric quantities. The use of an excess of organic carbonates however is preferred since it can serve as the organic solvent.

The type of catalyst used in step (1) is not critical. Suitable catalysts include heterogeneous base catalysts. A preferred class of catalysts however are metal based catalysts.

Organic or inorganic salts including, for example, acetates, chlorides, nitrates, propionates, isopropanoates, butanoates, 2-ethylhexanoates, n-octoates, isononanoates, benzoates, chlorobenzoates, naphthenates, stearates, itaconates, pivalates, phenolates, acetylacetonates, alkoxides, C₁₆/C₁₈-alkenylsuccinoates (ASA), C₁₂-alkenylsuccinoates (DSA), and the like, of metals 5 may be used.

Preferred are alkanoates having from 1 to 15 carbon atoms.

Suitable catalysts include, for example, zinc catalysts such as zinc chloride, zinc acetate, zinc nitrate, zinc propionate, zinc octoate, zinc benzoate, zinc p-chlorobenzoate, zinc naphthenat , 10 zinc stearate, zinc itaconate, zinc pivalate, zinc phenolate, zinc acetylacetonate, zinc methoxide, lead catalysts like lead acetate, lead nitrate and lead octoate, and tin catalysts like stannous chloride, stannous octoate, and mixtures thereof.

Preferably, the metal in the catalyst is selected from the group consisting of Ti, Zr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Pb, Bi and Cd.

15

The catalyst in step (1) is generally used in amounts between 10⁻³ and 20 mole% based on the amount of amines used.

The reaction conditions in step (1) largely depend on the type of reactants used, but are chosen so that substantially all of the amines are converted into a mixture of carbamates and alcohols.

20

Step (1) may be carried out at atmospheric or superatmospheric pressures.

The reaction time for step (1) will normally not exceed 5 hours. Reaction times of less than 3 hours are common, and reaction times of less than 2 hours have been achieved without any 25 problem.

Generally, the reaction temperature in step (1) will be between 50 and 300°C. Preferably, the method of the invention is carried out at temperatures between 100 and 250°C.

The catalyst needs to be removed from the reaction mixture before initiating step (3). It may be 30 removed continuously during, or after the termination of step (1) by any suitable method. A preferred separation method for step (2) is filtration.

Apart from the catalyst, any excess reactants and/or by-products from step (1) may need to be removed as well before proceeding to step (3).

35 The type of organic isocyanates obtained in step (3) depends on the type of the amine compound

used in step (1) and may be monomeric, di- or polymeric isocyanates.

Representative monomeric isocyanates which may be formed include methyl isocyanate, ethylisocyanate, isopropylisocyanate, isobutylisocyanate, hexylisocyanate, cyclohexylisocyanate, laurylisocyanate, stearyl isocyanate, phenylisocyanate, 4-chlorophenylisocyanate, 5 2-fluorophenylisocyanate, 3,4-dichlorophenyl isocyanate, tolylisocyanate and diisopropylphenylisocyanate.

Examples of difunctional isocyanates which can be made according to the present method include diphenylmethane diisocyanates such as 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 2,2'-diphenyl methane diisocyanate and mixtures thereof, toluene diisocyanat s
10 such as 2,4-toluene diisocyanate, 2,6-toluene diisocyanate and mixtures thereof, m-phenylene diisocyanate, 1,4-butylene diisocyanate, 1,6-hexylene diisocyanate, 1,5-naphthylene diisocyanate, 1,4-cyclohexylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 1,4-xylylene diisocyanate and isophorone diisocyanate.

Trifunctional and higher functional isocyanates which can be made include 2,4,6-toluene
15 triisocyanate and polymethylene polyphenylene polyisocyanates.

As already mentioned above, any mixtures of mono-, di- and polyfunctional isocyanates may be obtained depending on the composition of the starting amine compound.

In step (3) a solution of the carbamate formed in step (1) in the organic solvent is subjected to thermal decomposition.

20 Suitably between 1 and 20 % by weight of carbamate is present in the solution for carrying out step (3).

If however the amount of said solvent is insufficient to form a solution having a carbamate-concentration within the above range, addition of a suitable amount of an inert organic solvent, which may be the same or different, may be required.

25 In a preferred embodiment, the solvent is the organic carbonate used in the reaction of step (1).

However, any solvent or mixture of solvents which is inert to the reactants under the reaction conditions may be employed.

on has 30 Suitable solvents which may be employed include, for example, aromatic hydrocarbons such as benzene, halogenated aromatic hydrocarbons, such as monochlorobenzene, ortho-dichlorobenzene or 1-chloronaphthalene, alkylated aromatic hydrocarbons like toluene,

xylene, ethylbenzene, cumene or tetrahydronaphthalene, other functionalised aromatic hydrocarbons such as anisole, diphenylether, ethoxybenzene, benzonitrile, 2-fluoroanisole, 2,3-dimethylanisole or trifluorotoluene, alkanes such as n-pentane, n-hexane, n-heptane or higher or branched alkanes, cyclic alkanes like cyclopentane, cyclohexane or derivatives thereof, 5 halogenated alkanes like chloroform, dichloromethane, carbontetrachloride, and alkanes with other functional groups like diethylether, acetonitrile, dioxane or mixtures thereof, and the like.

The use of low boiling solvents in step (3) is advantageous as it facilitates the removal by distillation afterwards.

Preferred solvents other than the organic carbonate used in step (1) comprise 10 monochlorobenzene or ortho-dichlorobenzene.

In a process where a different inert organic solvent needs to be added for the above stated purpose, the excess organic carbonate remaining after step (1) may be removed before initiating step (3).

15 The reaction conditions in step (3) depend on the type of reactants used and the type of solvent.

The process may be carried out at atmospheric or superatmospheric pressures.

The reaction time for step (3) is dependent on the temperature and on the type and quantity of the 20 carbamate compound, but will normally not exceed 5 hours. Reaction times of less than 3 hours are common, and reaction times of less than 2 hours have been achieved without any problem.

The reaction temperature in step (3) is generally between 100 and 400 °C, preferably between 200 and 300 °C.

The distillation in step (4) can be conducted in any distillation apparatus which can be equipped, if 25 required, with heating and/or cooling means to keep the temperature within the desired range.

If the alcohol and the organic carbonate are present in such ratio that an azeotropic mixture is formed, the subsequent removal of any alcohol is greatly facilitated.

The process of the present invention may be conducted batchwise or as a semi-continuous or 30 continuous process.

The isocyanates and alcohols obtained by this process are generally of high purity and no additional treatment is required to further purify said products.

However, if a particularly high grade of purity is required, the reaction products formed may be subjected to known purification methods, such as filtration, extraction, or crystallisation or distillation.

The invention is illustrated by the following example.

5

Example

The methyl urethane of polyphenylene polymethylene polyamine was prepared as follows:

polyphenylene polymethylene polyamine (4.8 g; 24.2 mmol) was weighed into a clean dry glass liner. The solid was then dissolved in o-dichlorobenzene (ODCB)(80 ml) and dimethyl carbonate 5 added (21.6 g; 240 mmol) along with the catalyst (lead octoate as an 18 % w/w solution in mineral oil; 1.04 g equivalent to 0.9 mmol Pb). The glass liner was then placed inside a standard 300 ml stainless steel autoclave and the autoclave sealed. The reaction vessel was then purged with nitrogen and the contents heated to 180 C for 2 hours. At the end of the reaction period the contents were cooled and recovered. Four identical experiments were carried out and the crude 10 product solutions bulked together for post reaction treatment.

The solution was filtered to remove catalyst residues and the excess dimethyl carbonate and any residual methanol by-product were stripped from the crude mixture in vacuo. The resulting solution was washed with aqueous HCl (1 M/l) then washed twice with water before being dried over magnesium sulphate.

15 The yield was 10 g of polymethylene polyphenylene poly(methylurethane) as a 2% w/w solution in ODCB.

200 ml of the above solution was transferred to the thermolysis reactor. The reactor was sealed and purged with nitrogen. The polymethylene polyphenylene poly(methylurethane) was thermolysed at 250 C for 45 mins at 5 bar pressure with a nitrogen purge equivalent to 1 l/min. 20 ODCB solvent distilled from the reactor at a rate of 10 g/min and this was replaced at the same rate with fresh solvent.

The resulting polymethylene polyphenylene polyisocyanate was recovered by distillation of the solvent yielding a crude product with an NCO_w of 9.4 % w/w.

Claims

1. Process for the production of organic isocyanates comprising the following steps :
 - (1) reacting an amine compound with an organic carbonate in the presence of a catalyst and an organic solvent;
 - 5 (2) removing the catalyst;
 - (3) thermally decomposing the solution of the carbamate formed in step (1) in said organic solvent; and
 - (4) separating the organic solvent/alcohol mixture thus obtained from the organic isocyanate formed in step (3) by distillation.
- 10 2. Process according to claim 1 wherein the removal of the catalyst in step (2) is carried out by filtration.
3. Process according to claims 1 or 2 wherein the catalyst is a metal based catalyst.
4. Process according to any one of the preceding claims wherein the organic solvent is the organic carbonate used in the reaction of step (1).
- 15 5. Process according to any one of claims 1 to 3 wherein the organic solvent is an inert organic solvent different from the organic carbonate used in the reaction of step (1).
6. Process according to claim 5 wherein the inert organic solvent comprises monochlorobenzene or ortho-dichlorobenzene.
7. Process according to any one of the preceding claims wherein step (1) is carried at a
20 temperature of between 100 and 250 °C.
8. Process according to any one of the preceding claims wherein step (3) is carried at a temperature of between 200 and 300 °C.

9. Process according to any one of the preceding claims wherein the amine compound in step (1) comprises diaminodiphenylmethanes or polyaminopolyphenylmethanes or mixtures thereof.
10. Process according to any one of claims 1 to 8 wherein the amine compound in step (1) comprises toluenediamines.
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INTERNATIONAL SEARCH REPORT

Application No

PCT/EP 98/03224

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C263/04 C07C265/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (names of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 520 273 A (BAYER AG) 30 December 1992 see claims; examples ---	1
A	EP 0 510 459 A (BAYER AG) 28 October 1992 see claims; examples ---	1
A	US 5 315 034 A (MIZIA FRANCO ET AL) 24 May 1994 cited in the application see column 4, line 66 - column 6, line 54 ---	1
A	EP 0 323 514 A (DAICEL CHEM) 12 July 1989 cited in the application see claims; examples ---	1
A	DE 44 13 580 A (BAYER AG) 26 October 1995 cited in the application see claims; example 2 -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Information on patent family members

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